The Structure of the Band Spectrum of Helium.

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[PLATE 1.]

Introductory.

The band spectrum of helium was first described by Goldstein* and by the present writer† in 1913. The accounts given of the spectrum, and of the conditions favouring its production, were closely similar, but in neither case was any analysis of its structure attempted. In view of the somewhat complex character of the spectrum in certain regions, it appeared advisable for this purpose to secure a series of high dispersion plates, while the apparently abnormal nature of many of the bands provided a further incentive to their study on the largest scale possible. Accordingly, a number of exposures were made in the first, second, and third orders of the 10-foot concave grating of the Royal College of Science, London. Of these plates some seven or eight were suitable for measurement, only one of which, however, was in the third order. The outbreak of the War prevented the completion of the series of exposures contemplated, but sufficient material was accumulated to permit of a reasonably complete investigation of the spectrum between the limits 6480 — 3350 Å. A preliminary examination of these plates was made by Prof. Fowler‡ in 1914 (the author being on military service), and resulted in the detection of two series of double-headed bands presenting certain unusual features, of which the most striking was their distribution according to a line-series law. Nicholson,§ using Fowler's measures, calculated new formulæ for these series, and concluded that they were analogous to principal series in line spectra. No other work relating to the structure of the spectrum seems to have been published.

Apart from the doublet bands studied by Fowler, the most prominent features of the spectrum are a red band near λ 6400 and a green band near λ 5730, both of which appear, under moderately high dispersion, to have a quite abnormal structure. As these two bands seemed to promise more immediately interesting results than the remainder, they were the first to be studied, a band in the blue (near λ 4550), which appeared to be related to λ 6400, being subsequently included in the investigation. The results obtained in connection with these three bands form the subject of the present communication. The structure of the remainder of the spectrum, including Fowler's doublet bands, will be discussed, it is hoped, in a future paper.

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* 'Verh. Deutsch. Phys. Gesell.,' vol. 15, p. 402 (1913).

† 'Roy. Soc. Proc.,' A, vol. 89, p. 146 (1913).

‡ 'Roy. Soc. Proc.,' A, vol. 91, p. 208 (1915).

§ 'Roy. Soc. Proc.,' A, vol. 91, p. 432 (1915).

Detailed analysis of the three bands in question soon confirmed the opinion that their structure was strikingly different from that of "ordinary" bands, as may readily be seen by reference to the plate. In each case there is one series (two in λ 5730) which proceeds to a head, and several others which do not. The latter usually occur in pairs situated on either side of the former, and exact measurement and calculation suggest that each pair may be regarded as forming one series, of which several lines (usually two) near the middle are missing.

So far as was known these anomalous features had no counterpart in any other spectrum, with the possible exception of the ammonia band at λ 3360. Fowler's* photographs and diagrams of this band show some striking resemblances to the helium bands under consideration, but the analysis of the former is more difficult, partly because it is composed of triplets, and partly because, by reason of its situation in the ultra-violet, the wave-numbers are very sensitive to errors in wave-lengths. But it is thought that some at least of the results here obtained may assist in the interpretation of the structure of the ammonia band.

The main characteristics outlined above had been established early in 1919, and as there seemed little promise of further progress with the somewhat limited data available, experimental work† was undertaken, with a view to obtaining fresh information relating to the structure of the spectrum as a whole. That is to say, it was hoped to decompose the spectrum into families of bands and then to investigate the arrangement of the members of each family. By varying the conditions of pressure and electrical excitation distinct evidence of changes of relative intensity, and even of the production of new bands, was obtained, but before work along these lines had progressed very far some recent theoretical work on band spectra came to the author's notice, and was found to have an immediate bearing on the present problem. It appeared that this theory was not only capable of accounting for the apparent anomalies of structure and of exhibiting the manner in which these and ordinary bands are related, but also yielded information of a quantitative character concerning the structure of the molecules and atoms which emit the radiation. An excellent résumé of the work in question will be found in Sommerfeld's 'Atombau und Spectrallinien' (Vieweg, Braunschweig, 1921), pp. 550–566; a short account is also given in a recently published monograph on 'Series Spectra,' by N. R. Campbell (Camb. Univ. Press, 1921). As the treatment here adopted differs slightly from Sommerfeld's, it has been thought advisable, in order to render what follows intelligible, to give a brief outline of the theory before discussing its application to the helium bands.

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* 'Phil. Trans.,' A, vol. 218, p. 351.

† Aided by a grant from the Government Grants Committee of the Royal Society, and by a generous gift of helium from Lord Rayleigh.

The Quantum Theory of Band Spectra.

In conformity with a great deal of experimental evidence the theory attributes band spectra to molecules; these are treated (in the first instance) as rigid bodies possessing internal and rotational energy, either or both of which may vary, giving rise to emission or absorption of energy in the form of radiation. The former case is alone considered here. The fundamental assumptions are those employed by Bohr in his theory of line series, and now generally recognised as of wide validity, viz.:—

(1) The emission of a frequency ν is due to a decrease $h\nu$ in the energy of the radiating system.

(2) If the system is in rotation and is not emitting radiation its angular momentum must be an integral multiple of $h/2\pi$. There is thus a limited number of possible angular velocities, just as in Bohr's model of the hydrogen atom there is a limited number of stationary electron orbits.

Let I and ω respectively represent the moment of inertia (about the axis of rotation) and the angular velocity of the molecule. Then if the rotation quantum number m changes to m' $(m' < m)$, the energy radiated

$$= h\nu = \tfrac{1}{2}\mathrm{I}\omega^2 - \tfrac{1}{2}\mathrm{I}\omega'^2 \text{ by (1).}$$

But

$$\mathrm{I}\omega = \frac{mh}{2\pi} \text{ by (2).}$$

Thus

$$h\nu = \frac{1}{2\mathrm{I}}\left\{\left(\frac{mh}{2\pi}\right)^2 - \left(\frac{m'h}{2\pi}\right)^2\right\} = \frac{h^2}{8\pi^2\mathrm{I}}(m^2 - m'^2).$$

According to the selection principle of Rubinowicz m cannot change by more than one unit at a time, so that we shall have

$$\nu = \frac{h}{8\pi^2\mathrm{I}}(2m-1).$$

This represents a series of equally spaced lines, and from existing data in connection with molecular moments of inertia (of the order of 10^{-40} for the lighter molecules) we conclude that they must lie in the far infra-red, round about 30μ. In spite of the great difficulties attending work in this region a certain amount of evidence confirmatory of the theory has been obtained (*e.g.*, for water-vapour absorption by Rubens and by v. Bahr), but accurate measurements are not possible at present. If, however, we suppose, as Schwarzschild suggested, that a change in the configuration of the molecule involving a decrease $h\nu_0$ in the internal energy may occcur simultaneously with the change in angular momentum, the resultant frequency radiated may be very much greater than those characterising the pure rotation spectrum, so that it may be brought into the region where spectroscopic investigation is more easily and accurately conducted than in the far infra-red.

The configuration change referred to may primarily concern the positions of the electrons or of the atoms within the molecule. In the former case the consequent alterations in the electrical forces are bound to affect the distance apart of the atoms, so that in both cases the final moment of inertia will differ in general from the initial. Thus, if the moment of inertia takes the value I′ after the configuration change, we shall have

$$h\nu = h\nu_0 + \frac{h^2 m^2}{8\pi^2 \mathrm{I}} - \frac{h^2 (m-1)^2}{8\pi^2 \mathrm{I}'} \qquad [m \rightarrow (m-1)$$

whence $$\nu = \nu_0 - \frac{h}{8\pi^2 \mathrm{I}'} + \frac{h}{4\pi^2 \mathrm{I}'} \cdot m + \frac{h}{8\pi^2}\left(\frac{1}{\mathrm{I}} - \frac{1}{\mathrm{I}'}\right) m^2,$$

or writing $c_0{}'$ for $\dfrac{h}{8\pi^2 \mathrm{I}'}$ and c_2 for $\dfrac{h}{8\pi^2}\left(\dfrac{1}{\mathrm{I}} - \dfrac{1}{\mathrm{I}'}\right)$,

$$\nu = \nu_0 - c_0{}' + 2c_0{}'m + c_2 m^2.$$

Two other cases are also possible. First, the angular momentum may remain unaltered during the change $h\nu_0$. The frequency emitted will, however, be modified in consequence of the change in the moment of inertia, so that

$$\nu = \nu_0 + c_2 m^2 \qquad [m \rightarrow m.$$

Finally,* the rotation quantum number may increase from $(m-1)$ to m, giving

$$\nu = \nu_0 + c_0 - 2c_0 m + c_2 m^2 \qquad [(m-1) \rightarrow m$$

where c_0 denotes $\dfrac{h}{8\pi^2 \mathrm{I}}$.

Evidently $$c_0 - c_0{}' = c_2.$$

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* Here the treatment departs slightly from that of Sommerfeld, who considers the change $m \rightarrow (m+1)$, and thus obtains an expression identical with the first, except that the coefficient of m is negative (*i.e.*, $-2c_0{}'$), so that both series are represented by one formula in which m takes both positive and negative values. The method adopted in the text has the advantage of making the numbering symmetrical, *i.e.*, lines associated with the same two quantum states are denoted by the same value of m in the formulæ, whereas by Sommerfeld's treatment they are denoted by $+m$ and $-(m+1)$. Further,

Adopting the notation of Heurlinger we shall write R(m), Q(m) and P(m) respectively, for the general term of each of these series. Thus for the

$$\text{positive branch } R(m) = \nu_0 - c_0' + 2c_0'm + c_2m^2,$$

$$\text{null (zero) ,, } Q(m) = \nu_0 + c_2m^2,$$

$$\text{negative ,, } P(m) = \nu_0 + c_0 - 2c_0m + c_2m^2.$$

Only positive integral values are to be given to m.

Graphically interpreted these equations represent a system of similar parabolas having their axes parallel to the ν axis. The vertex of the Q parabola is on the ν axis, and the vertices of the P and R parabolas are nearly equidistant from it and on opposite sides. The latter curves are, in fact, reflections of one another in the line $m = \frac{1}{2}$.

A typical set of series is represented in fig. 1; they have been calculated for the case when $c_0 = 15{\cdot}5$ ($cm.^{-1}$), $c_0' = 14{\cdot}5$ and accordingly $c_2 = +1$, values which are not far removed from those found in connection with the helium bands. The lower part of the diagram illustrates the actual appearance of the bands on a uniform scale of wave-numbers, except that to avoid confusion the Q series has been plotted separately from the other two, and the two series proceeding from the P head have also been separated.

If c_2 had been negative (corresponding to $I' > I$) a similar set of series would have been obtained, but degraded in the opposite direction, *i.e.*, to the less refrangible side. Further, the R series and not the P series would then have proceeded to a head.

On this theory the head of a band assumes only a secondary importance in comparison with the frequency ν_0; it is merely a region where the lines happen to be crowded together, and its location is of no primary significance in connection with the structure of the band. For example, in seeking relationships between different bands, it is to be expected that the laws expressing these will take their simplest form when they are formulated in terms of the respective values of ν_0, instead of the frequencies of the heads. For series of the Q type the distinction is unnecessary, since the head is at

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the former method was thought to be more convenient for testing the applicability of the theory, since the empirical representation of both series in a single formula would have necessitated the employment of higher powers of m than would be required in the separate treatment of the two series, so increasing considerably the labour of computation. But the numbering adopted by Sommerfeld has been generally used, and for that reason is possibly to be preferred.

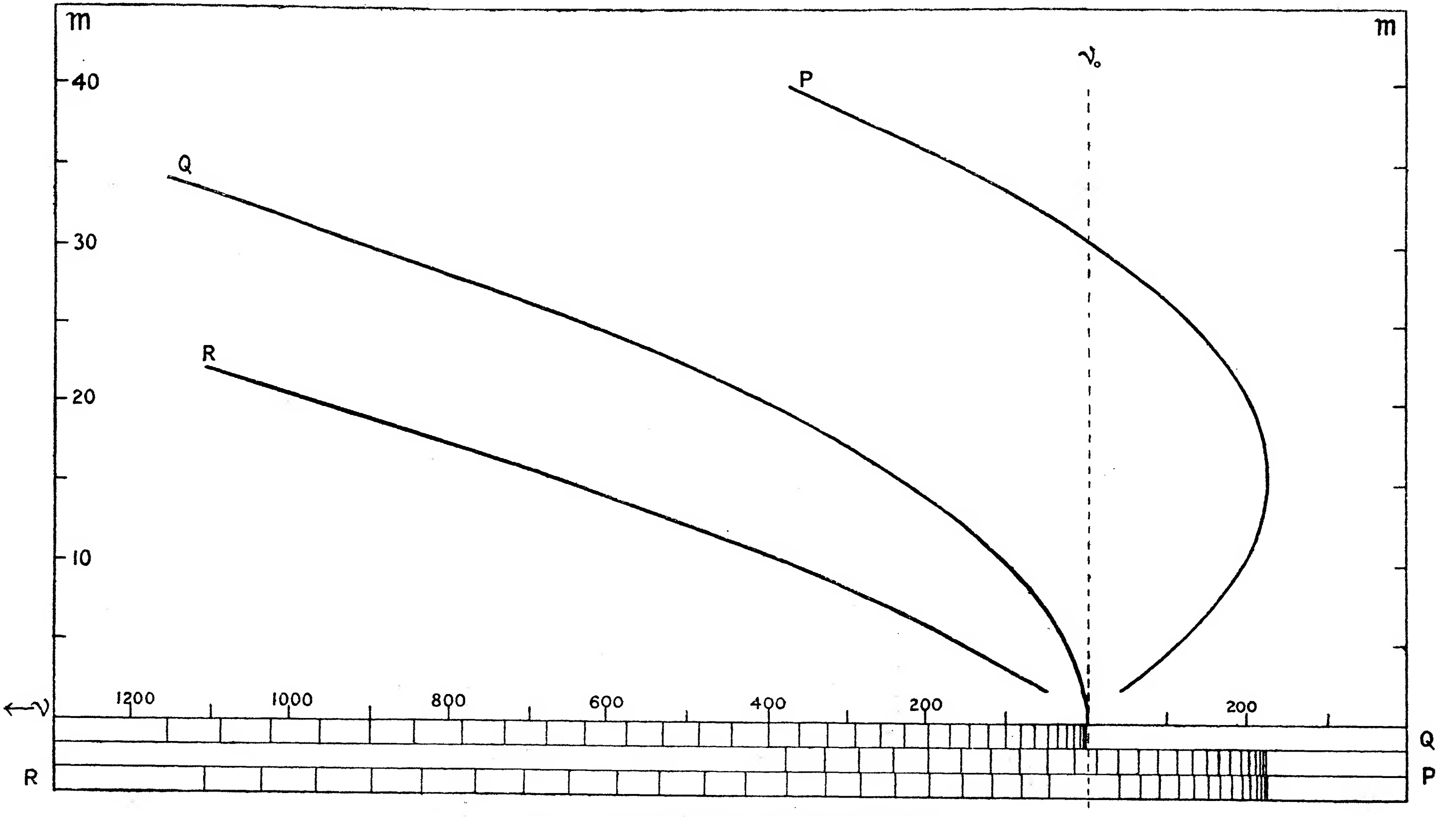

FIG. 1.—Theoretical group of band series.

$R(m) = \nu_0 - c_0' + 2c_0'm + c_2m^2$; $Q(m) = \nu_0 + c_2m^2$; $P(m) = \nu_0 + c_0 - 2c_0m + c_2m^2$; $c_0 = 15{\cdot}5$, $c_0' = 14{\cdot}5$; $c_2 = c_0 - c_0' = 1{\cdot}0$ cm.$^{-1}$.

ν_0, but the head of the P or R series (whichever may happen to possess one) may be shown to be given by

$$m = \frac{c_0}{c_2}\text{ (P series)} \quad \text{or} \quad -\frac{c_0'}{c_2}\text{ (R series)}$$

and
$$\nu = \nu_0 - \frac{c_0 c_0'}{c_2},$$

i.e.,
$$\nu = \nu_0 + \frac{h}{8\pi^2(\mathrm{I}-\mathrm{I}')}.$$

It may be noted that the term "head" as here employed refers to the vertex of the parabola, which does not necessarily correspond with an actual line, and indeed will in general not do so.

Many of the characteristics of band structure outlined above were recognised by Heurlinger* independently of the theory, and he and others have subsequently shown that the structure of many typical bands (*e.g.*, nitrogen and "cyanogen") may be interpreted by its aid, provided certain modifications are made in some cases. For example, the Q series is frequently absent, and there may be six or twelve series in all, instead of three, but as these complications do not occur in helium they need not be considered here, One feature which is common to all the bands studied must, however, be mentioned, namely, the gap (indicated in the figure) which occurs between the P and R series. The fundamental frequency ν_0 is invariably absent from the spectrum, and often one or more of the adjacent lines are also suppressed. The absence of the former has been attributed to the non-existence of molecules having no rotational energy, which would obviously be the only ones capable of giving rise to it, and this view is not without some support on other grounds (*e.g.*, investigations on the specific heat of hydrogen at low temperatures). This explanation would at the same time account for the absence of the adjacent lines P(1) and R(1), for these are due to the transitions $0 \rightarrow 1$ and $1 \rightarrow 0$. These lines are, in fact, absent from the helium bands so far studied, and have therefore been omitted from fig. 1. But it appears that the above explanation fails in the case of the "cyanogen" band at λ 4216, where ν_0 is absent, but the pair of lines given by $m = 1$ actually occurs. We may perhaps, in this and similar cases, infer that the non-rotating molecule is capable of existing, but incapable of emitting its characteristic frequency ν_0 without a simultaneous change in its angular momentum. In this connection Lenz† has proposed to introduce a second quantum number n, which relates to the angular momentum about an axis perpendicular to that associated with m. For example, in the Bohr-Debye model of the hydrogen molecule n would refer to rotation about the axis of figure (the line joining the atoms) and m to that about a perpendicular axis through the centre of gravity of the atoms. He thus obtains a formula

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* 'Untersuchungen über die Structur der Bandenspektra,' Diss. Lund., 1918.

† 'Verh. d. Phys. Ges.,' vol. 31, p. 632 (1919).

$$\nu = \nu_0 + c_1(m+n) + c_2(m+n)^2$$

in which m can take all possible integral values, but n can never be less than a certain minimum value dependent upon the structure of the molecule (*e.g.*, if there are two electrons revolving in an orbit perpendicular to the axis of figure, n could never be less than 2). Evidently in such a case the first n_0 lines will be missing from each of the P and R series, n_0 denoting the above-mentioned minimum value of n.

The actual appearance of the bands originating in this manner will be determined not only by the location of the lines but also by their intensities. These depend upon the way in which the various possible angular velocities are distributed amongst the molecules. Theory indicates some general features of this distribution which appear to be in accordance with observation, although precise measurements of intensities have not been made. Thus, for example, as m increases the intensities increase pretty rapidly, reach a maximum and then decline much more slowly. Also, the greater the moment of inertia of the molecule the greater will be the proportion of molecules possessing large angular momenta; in other words the number of lines of observable intensity will be greater. Increase of temperature will produce a similar effect.

In conclusion, the special characteristics which might be anticipated for the helium bands (as compared with those due to heavier elements and compounds) may be indicated. Whatever the constitution of the molecule responsible for their production, it is likely that its moment of inertia will be relatively small, considerably smaller than, say, that of the nitrogen molecule, so that the frequency intervals between the lines in the neighbourhood of ν_0 should be relatively large, since these are (approximately) inversely proportional to I. Further, the series will comprise comparatively few members, and may in the case of the P and R branches fade into invisibility before the head is reached, so causing a conspicuous difference in appearance from that of an "ordinary" band series, in which the head is the most prominent feature. These expectations are found to be realised in the case of the three bands under examination, and their anomalous character in these respects is thus seen to be only apparent.

The Band λ 6400.

The general appearance of this band will be seen from the Plate, and the manner in which it has been analysed is shown in fig. 2, which is a graphical representation on a scale of wave-numbers, intensities being also indicated.

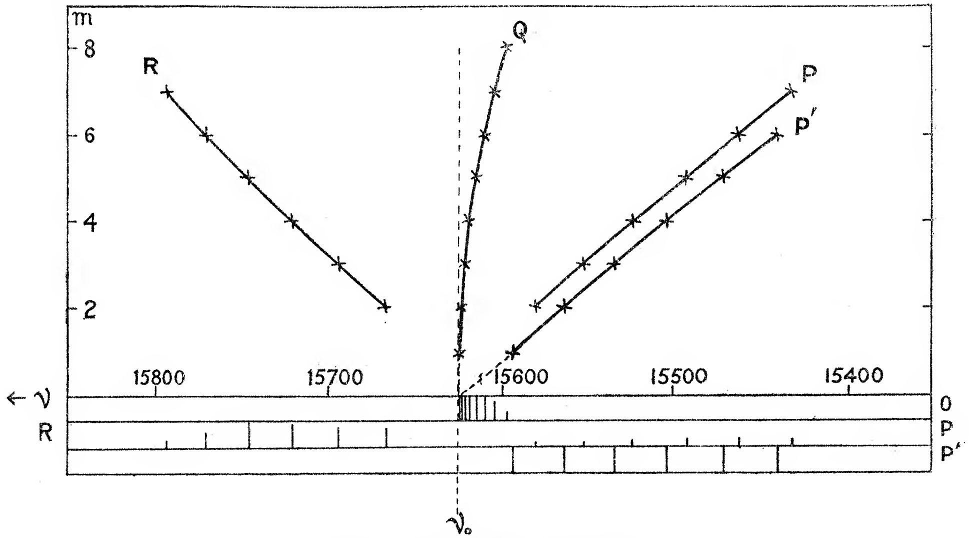

Fig. 2.—Helium band at λ 6400.

Full details of the band are collected in Table I, which gives the estimated intensities, wave-lengths (I.A., air) and wave-numbers (*vacuo*) of all the lines of the four series recognised. These were obtained from a first-order grating plate which had an exposure of about 6 hours on the bulb of a Plücker tube containing helium at a few millimetres pressure (estimated) and excited by an oscillatory discharge of moderate intensity. The absolute wave-lengths are not very reliable, on account of the liability to temperature shift during an exposure of this length, and may be in error by 0·1 Å. or so (as estimated from previous experience of the instrument). But for the present purpose such a shift, so long as it is reasonably small, is of little importance. Relatively to each other the wave-lengths should be accurate within the limits of measurement, which is estimated (by comparison of different sets of measures) at about 0·02 Å., corresponding to 0·05 unit in the wave-number. The estimates of intensity were made at the first measurement (in 1914) before the allocation into series, and were not subsequently revised (only checked). The wave-lengths of Burns* were used for the iron arc comparison lines, and the Bureau of Standards Tables† for the reductions to vacuum.

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* 'Lick. Obs. Bull.,' No. 247, 1913.

† 'Scientific Paper,' No. 327, 1918.

Table I.—Details of the Band λ 6400.

	R series.			Q series.		
m.	Int.	λ (air).	ν (vac.).	Int.	λ (air).	ν (vac.).
1				10	6398·74	15623·77†
2	8	6381·21	15666·68	10	99·26	22·50
3	8	70·02	94·21	10	6400·02	20·64
4	9	59·22	15720·88	10	01·19	17·79
5	10	48·89	46·44	10	02·73	14·04
6	6	39·06	70·86	10	04·62	09·43
7	3	29·80	93·93	8	06·85	03·99
8				3†	09·48	15597·58

	P series.			P′ series.		
m.	Int.	λ (air).	ν (vac.).	Int.	λ (air).	ν (vac.).
1				10	6410·79	15594·39
2	1	6415·92	15581·92	10	23·10	64·51
3	1	28·11	52·38	10	35·68	34·09
4	2	40·38	22·75	10	48·49	03·23
5	2	52·76	15492·96	10	61·47	15472·08
6	2	65·32	62·89	10	74·59	40·73*
7	2	78·12	32·31*			

* The next members of these series are just off the edge of the plates available for accurate wave-length determinations, but several more appear on plates taken with other instruments of less dispersion.

† This line might alternatively be regarded as the first of the P′ series, but as the corresponding lines of the 5730 and 4546 bands are certainly Q (1) in each case this has been designated Q (1) also.

Formulæ were next calculated for the four series. Examination of the second differences showed that the wave-numbers could not be represented by a formula of the type $\nu = a+bm+cm^2$, but that at least one additional term of higher order would be required. A third order term was introduced, and was found to be sufficient for a satisfactory representation in all cases. The coefficients were calculated by the method of least squares, and are exhibited in Table II, which also gives the corresponding residuals.

The similarity between the disposition of the series designated P, Q and R and that of the theoretical family illustrated in fig. 1 is apparent from the figure, and we see at once that the unusual appearance of this band is chiefly due to the small number of lines developed, so that the head which would be expected in the R series cannot be observed. The extreme faintness of the P series and the presence of a very strong additional series (P′) are other circumstances which help to disguise the true character of this band, but the calculations which follow leave no doubt that the structure is in the main identical with that required by the theory.

Table II.

Coefficients in Formulæ for λ 6400 Series. Residuals.

Series.	m^0.	m.	m^2.	m^3.	(O – C) × 100.							
					1.	2.	3.	4.	5.	6.	7.	8.
R	15609·61	+29·045	−0·2015	−0·02667		0	−1	+2	−2	−1	+2	
Q	15624·08	+0·066	−0·4004	−0·00273	+3	−9	+4	+3	−2	−4	0	0
P	15641·38	−30·005	+0·1805	−0·02300		+1	+2	−3	−2	0	+1	
P′	15623·73	−28·951	−0·3662	+0·01798	−5	0	+2	0	0	0		

Theoretical formulæ :—

$\mathrm{R}(m) = \nu_0 - c_0' + 2c_0'm + c_2m^2.$

$\mathrm{Q}(m) = \nu_0 + c_2m^2.$

$\mathrm{P}(m) = \nu_0 + c_0 - 2c_0m + c_2m^2.$

$\mathrm{P}'(m)$ (see p. 50).

From Table II it will be seen that third power terms appear in the formulæ; they are in fact necessary for the representation of the series, and must correspond to some factor not taken into account in the theory as presented above, a factor which we shall for convenience refer to as the "perturbation" without enquiring at present into its nature. There may of course be more than one such factor, but their total effect on ν may be represented by a function $a+bm+cm^2+dm^3$ which when added to the simple second-order theoretical formula gives the empirical formula actually obtained. The coefficient of m^3 in the latter is equal to d, but the values of a, b and c cannot be determined, and therefore the relations which should theoretically exist between the coefficients of m^0, m and m^2 are not likely to be exactly satisfied, so that a complete verification of the theory is not to be expected.

Proceeding now to compare coefficients of the theoretical and experimental formulæ, we obtain,

(1) From P, $\nu_0+c_0 = 15641{\cdot}38, \quad c_0 = 15{\cdot}00, \quad \therefore \nu_0 = 15626{\cdot}38,$

„ R, $\nu_0-c_0' = 15609{\cdot}61, \quad c_0' = 14{\cdot}52, \quad \therefore \nu_0 = 15624{\cdot}13.$

The difference between the two values of ν_0 is presumably due to the coefficients a and b of the function expressing the perturbation, and is small enough to justify the application of the theory to these series, particularly as the value of ν_0 derived from the Q series, *i.e.*, 15624·08, is also in agreement.

(2) The second theoretical relation between the coefficients of the three formulæ is that c_2, the coefficient of m^2, should be the same for all, and equal $(c_0 - c_0')$. To test this, we have—

from P and R, $c_0 - c_0' = +0{\cdot}48$,
" R $c_2 = -0{\cdot}20$,
" Q $c_2 = -0{\cdot}40$,
" P $c_2 = +0{\cdot}18$.

The expected relation is not established, but the terms in question are so small that the perturbation is probably relatively important in this case. The disagreement indicates that the values obtained above for c_0 and c_0' may not be very reliable, within perhaps 3 per cent. or so.

Taking them for what they are worth, however, the corresponding moments of inertia may be calculated, with the following results:—

$$\text{Initial value } I = \frac{h}{8\pi^2 c_0} = 1{\cdot}84 \times 10^{-40} \text{ grm.-cm.}^2$$

$$\text{Final value } I' = \frac{h}{8\pi^2 c_0'} = 1{\cdot}90 \times 10^{-40} \text{ grm.-cm.}^2$$

where h has been taken as $6{\cdot}54 \times 10^{-27}$ erg-sec., and c_0, c_0' are expressed as frequencies (3×10^{10} times the previous values).

The Q series, it may be noted, conforms closely to the theoretical requirements in that the coefficients of m and m^3 are both very small. It is, therefore, capable of approximate representation by a parabola with vertex at $m = 0$, $\nu = \nu_0$, while $m = 1$ gives the first observed line. The absence of Q (0) is to be expected in view of the absence of P (1) and R (1), and supports the conclusion that the non-rotating molecule does not occur. The smallness of the perturbation in this case also allows the numeration to be determined without ambiguity, and suggests that the value of ν_0 deduced, viz., 15624·1, is probably the best that can be derived for these series.

The additional series P′ has no counterpart in the theoretical group of series, but is nevertheless intimately related to the three already dealt with. The nature of the relationship is readily seen from the figure, and may be expressed as follows:—

(1) P′ is approximately parallel to P, *i.e.*, the coefficients of m are of the same order of magnitude in both cases.

(2) P′ extrapolates to ν_0 derived from the Q series, *i.e.*, P′ (0) = Q (0) within the limits of experimental error. As a matter of fact, the line Q (1), 15623·77, would fit equally well in the P′ series as P′ (0), but the former identification is here preferred, because it agrees with that adopted for the

other bands studied, where the corresponding lines are certainly Q (1) and not P′ (0).

It may be noted that the numeration of this series cannot be definitely settled at present, since the mechanism of its production is not understood; that employed must therefore be regarded as provisional.

The formula representing this series will be seen to be of the form

$$P'(m) = \nu_0 - 2c'm + c_2'm^2,$$

where ν_0 is identical with that characteristic of the P, Q, and R series, and c', c_2' are not very different in magnitude from the corresponding coefficients of the normal family. Further discussion of this series may be postponed until the other two bands have been considered.

The Band λ 4546.

The details of this band are given in Table III. Again, only one plate suitable for measurement was available, and comparison of several independent sets of measures shows that the wave-numbers are probably less

Table III.—Details of the Band λ 4546.

	R series.			Q series.		
m.	Int.	λ (air).	ν (vac.).	Int.	λ (air).	ν (vac.).
1				3	4545 ·80	21992 ·21
2	3	4537 ·14	22034 ·15	4	46 ·21	90 ·20
3	3	31 ·71	60 ·54	6	46 ·93	86 ·75
4	3	26 ·66	85 ·15	6	47 ·91	82 ·00
5	3	21 ·92	22108 ·34	6	49 ·16	75 ·90
6	3	17 ·62	29 ·38	5	50 ·81	67 ·96
7	1	13 ·66	48 ·79	4	52 ·72	58 ·80
8				3	55 ·04	47 ·56

	P series.			P′ series.		
m.	Int.	λ (air).	ν (vac.).	Int.	λ (air).	ν (vac.).
1				4	4551 ·80	21963 ·20
2				6	58 ·20	32 ·35
3				6	64 ·82	00 ·56
4	0	4564 ·27	21903 ·2 ?	6	71 ·69	21867 ·63
5	1−	70 ·48	21873 ·42	6	78 ·75	33 ·92
6	1	76 ·98	42 ·36	6	85 ·97	21799 ·55
7	1	83 ·72	10 ·25	3	93 ·45	64 ·04
8	1	90 ·68	21777 ·19	1	4601 ·12	27 ·79
9	1	97 ·88	43 ·10			

The line P (4), marked ?, was too weak to measure satisfactorily, and the tabulated wave-number may be in error by 0 ·3 or so.

accurate than before, partly owing to the larger value of $d\nu/d\lambda$ in this region, and partly also on account of the slightly winged character of the lines (attributed to temperature shift during the 7 hours' exposure). It is believed that the relative errors in wave-number will seldom exceed 0·15 unit however. The P series was so faint that it could not be measured on the iron arc overlap, and the previously determined P′ lines were therefore utilised as standards. This procedure necessarily increased the probable error somewhat. A few lines (all faint) evidently not connected with the series have not been recorded.

Table IV exhibits the formulæ and residuals in the same manner as before. The accuracy of the wave-numbers did not justify the calculation of third power terms; in fact, quadratic formulæ sufficed for the representation of all the series except Q, where a further term would have been required to include the eighth member.

Table IV.

Coefficients in Formulæ for λ 4546 Series. Residuals.

Series.	m^0.	m.	m^2.	(O − C) × 100.								
				1.	2.	3.	4.	5.	6.	7.	8.	9.
R	21975·99	+30·818	−0·8761		+2	−2	−11	+14	0	−2		
Q	21992·64	+0·244	−0·7250	+6	−3	−9	−2	+17	−4	−2	(−63)	
P	22013·80	−25·571	−0·5007				(−30)	0	+2	−2	0	0
P′	21993·35	−29·640	−0·4449	−7	+4	+13	−4	−11	+5	−3	+3	

Residuals in brackets refer to lines not used in obtaining formulæ, *e.g.*, Q (8) is unreliable, as it is a blend with a stronger line.

From P, $\nu_0 + c_0 = 22013 \cdot 80$, $c_0 = 12 \cdot 79$, $\therefore \nu_0 = 22001 \cdot 0$.
" R, $\nu_0 - c_0' = 21975 \cdot 99$, $c_0' = 15 \cdot 41$, $\therefore \nu_0 = 21991 \cdot 4$.
" Q, $\nu_0 = 21992 \cdot 64$.

The similarity of this band to λ 6400 is apparent from fig. 3; both consist of a "normal" family of P, Q, and R series, the first being much weaker than the other two, together with a strong additional series (P′), running roughly parallel to the P series and commencing at the head of the Q series. Both families are degraded toward the less refrangible side, corresponding on the theory to a decrease in the moment of inertia of the molecule as a result of the configuration change.

It will be seen from Table IV that while the two values of ν_0 from Q and R agree very well, that from P is discordant by about 10 units. It should be noted, however, that this series was not completely observed: P (4) was too weak to measure reliably, P (3) would fall under P′ (2), and P (2) was not present. The value of ν_0 in the case of this series is therefore derived from a long extrapolation, namely, from P (5) to P (0), and is entitled to but little weight. A displacement of the series may possibly exist, but cannot be certainly established from the data available. As the coefficient of m is affected by a similar uncertainty, a better value of c_0 is probably obtainable from the well determined R series by utilising the theoretical relation $c_0 - c_0' = c_2$. We have $c_0' = 15{\cdot}4$, $c_2 = -0{\cdot}8$ (mean of Q and R values) whence $c_0 = 14{\cdot}6$. These values correspond to initial and final moments of inertia of $1{\cdot}89 \times 10^{-40}$ and $1{\cdot}79 \times 10^{-40}$ respectively. In view of the method by which these figures have been obtained, it would be inadvisable to attach too much weight to them, but it is probably justifiable to conclude that the average moment of inertia is of the order of $1{\cdot}8$ to $1{\cdot}9 \times 10^{-40}$. In the case of the band λ 6400 the average moment of inertia was found to be $1{\cdot}87 \times 10^{-40}$. This agreement lends further support to the view that these two bands are closely related in some way.

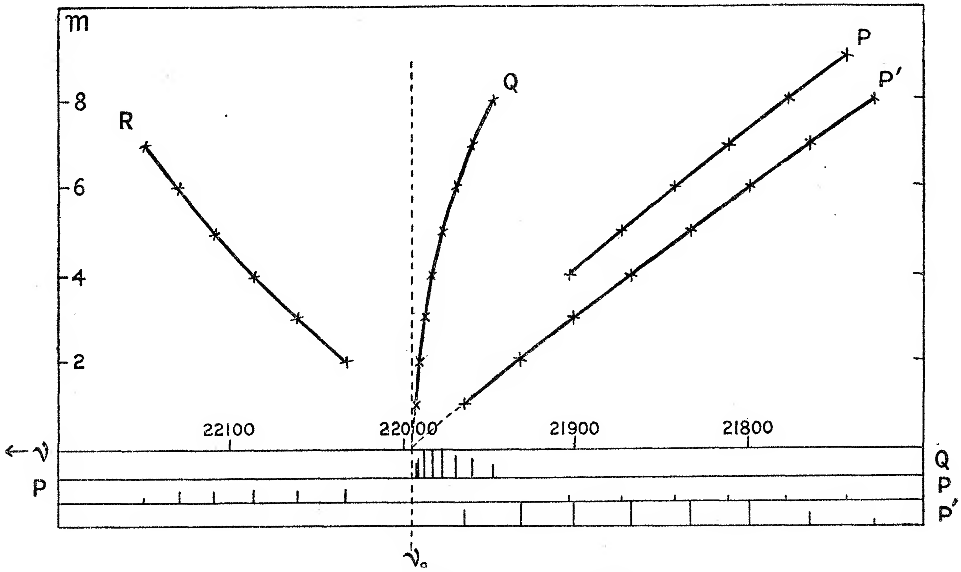

Fig. 3.—Helium band at λ 4546.

If the two bands were associated in the manner characteristic of line series, as found by Fowler (*loc. cit.*) for other bands in this spectrum, we should expect to find the next member near $\nu = 24820$, and it should be of observable intensity. On the plates available this region is a confused mass of lines in which no regularities have been established as yet, and it is possible that the hypothetical band may have escaped detection. At all events its absence cannot be proved. The next member might be expected at about 26320, with, of course, a rather large probable error. There is a weak single head at 26466, which is degraded towards the red and might from its appearance be associated with λλ 6400 and 4546, but on the high dispersion plates it is too weak to measure satisfactorily. It is hoped that further experimental work may throw some light on this question. Meanwhile, it may be remarked that there is just a possibility that the band at 26466 may be the third member of the series instead of the fourth. If this were the case the series law would be rather a curious one, namely, the squares of the frequencies would be approximately as 1 : 2 : 3, *i.e.*, the wave-numbers would be in the ratio $1 : \sqrt{2} : \sqrt{3}$. The exact figures are as follows:—

$$\nu_1 = 15624 = 1{\cdot}562 \times 10^4,$$

$$\nu_2 = 21992, \qquad \frac{\nu_2}{\sqrt{2}} = 1{\cdot}555 \times 10^4,$$

$$\nu_3 = 26466, \qquad \frac{\nu_3}{\sqrt{3}} = 1{\cdot}528 \times 10^4.$$

In this case the next member would fall at about $\nu = 30{,}000$, which is just outside the region covered by the plates.

The Band λ 5730.

This band is visually the most prominent feature of the spectrum, and differs from the remainder in being degraded towards the more refrangible side. It is rather more complex than the two bands already described, but the results established for these have been of great assistance in elucidating its structure. Again the measurements were all made on one plate (first order, 10 hours' exposure); the wave-lengths are probably reliable to about 0·02A, and the wave-numbers to 0·06 cm.$^{-1}$, in both cases relatively to each other. These particulars, with intensities and series allocation will be found in Table V, which also includes all lines which appear on the plate but have not been allocated to series. These cannot be traced to any impurity or accident (*e.g.*, ghosts, superposed orders), and some at least of them may prove to be associated with the band.

Six series have been recognised in this band, and the coefficients of the formulæ calculated for them are shown in Table VI. In several cases a fourth power term appeared to be required in order to secure a satisfactory representation, suggesting a rather larger perturbation than in the previous cases, although the slightly greater extension of these series is no doubt partly responsible.

Table V.—Details of the Band λ 5730.

Int.	λ (air).	ν (vac.).	Series.	Int.	λ (air).	ν (vac.)	Series.
1–	5645·87	17707·23	R (8)	3	5748·60	17390·74	
1–	50·93	17691·38	R′ (8)	1	49·15	89·08	
1	58·44	67·81	R (7)	2	50·17	86·00	
1	60·12	62·58	R′ (7)	1+	51·10	83·27	
2	70·07	31·59	R′ (6)	5	51·69	81·38	P′ (2)
2	71·13	28·28	R (6)	1	52·09	80·19	
3	80·50	17599·20	R′ (5)	1	52·84	77·93	
4	83·58	89·67	R (5)	1+	53·54	75·78	
5	91·27	65·92	R′ (4)	7	56·21	67·74	P (3)
6	95·64	52·44	R (4)	9	59·82	56·86	P′ (3)
1–	97·42	47·03		9	64·45	42·91	P (4)
6+	5702·13	32·44	R′ (3)	9	67·10	34·94	P′ (4)
1–	04·90	24·02		1	69·55	27·58	
7	07·15	17·03	R (3)	9	72·33	19·23	P (5)
1–	08·14	14·06		10	73·59	15·47	P′ (5)
7	12·91	17499·38	R′ (2)	1+	77·26	04·48	
1	14·58	94·15		8	79·29	17298·37	P_1' (6)
2	16·23	89·10	Q_1 (7)	8	80·09	96·00	P (6)
7	18·10	83·47	R (2)	5	84·38	83·16	P′ (7)
1–	18·77	81·43		1	85·31	80·37	
3	19·99	77·70	Q_1 (6)	3	86·95	75·57	
2	21·18	74·06		5	87·79	72·98	P (7)
2	21·98	71·64		3	89·00	69·35	P′ (8)
10	23·39	67·30	Q_1 (5) R′ (1) ?	2–	93·36	56·28	P′ (9)
3	24·86	62·85	Q_2 (6)	1	93·85	54·91	
9	26·66	57·35	Q_2 (5) Q_1 (4)	5	95·59	49·72	P (8)
7	28·58	51·50	Q_2 (4)	1	96·08	48·28	
7	29·27	49·41	Q_1 (3)	1	97·81	43·12	P′ (10)
7	30·39	46·00	Q_2 (3)	5	98·77	40·28	
6	31·25	43·38	Q_1 (2)	1–	02·24	29·96	
6	31·93	41·31	Q_2 (2)	1	03·19	27·12	
5	32·57	39·36	Q_1 (1)	2	03·64	25·81	P (9)
3	33·04	37·94	Q_2 (1)	1	09·91	07·20	
2	34·45	33·63		1	10·69	04·90	
2	39·35	18·75		1	11·97	01·12	P (10)
2	44·33	03·64		6	12·56	17199·42	
1	46·97	17395·67		1	16·39	88·09	
2	47·53	93·96	P (2)	1	19·25	79·65	
				1	20·67	75·46	P (11)

The relations found to exist between these six series are exhibited graphically in fig. 4 in the same manner as before. It may be well to point out, however, that the representation given in the figure and also the formula coefficients are to a large extent dependent upon the numeration adopted, and an alteration in the latter, which is in some cases open to question, would shift the series vertically in the diagram and considerably alter the appearance of the system. (See p. 56.)

Table VI.

Coefficients in Formulæ for λ 5730 Series. Residuals.

Series.	m^0.	m.	m^2.	m^3.	m^4.	(O−C) × 100.										
						1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
R	17420·56	+30·691	+0·0947	+0·16910	−0·012580		−1	0	−1	+3	−5	−2	+3			
Q_1	17437·29	+1·150	+0·8738	+0·05000	−0·006750	0	0	0	0*	+38†	0	0				
Q_2	17436·40	+0·448	+1·1740	−0·08567	—	0	0	0	+1	+7*	0					
P	17453·10	−32·333	+1·5760	−0·10008	+0·001380		0	+4	−2	+4	−1	0	−1	−4	+3	(+33)
R′	17436·76	+29·539	+1·0855	−0·09951	—	+1?	−1	−2	0	+5	0	−3	(−24)			
P′	17437·28	−29·988	+0·8703	+0·08410	−0·006542		+3	−3	−2	−5	0	+1	+1	+1	+1	

* Blend.

† May be a blend with R′ (1). Neglected in obtaining formula.

? This residual refers to Q_1 (5), the intensity of which seems abnormally high, suggesting that R′ (1) may possibly be superposed on it.

Residuals in brackets refer to very faint lines, the identification of which is not regarded as certain, and which have been disregarded in obtaining the formulæ.

The six series fall into three pairs, of P, Q and R types respectively, and at first sight it would appear natural to regard them as two complete normal families. There are several objections to this view however, the chief of which is that the two Q series converge almost to the same wave-number, whereas the two values of ν_0 derived from P, R and P′, R′ (see figure) differ by no less than 14 units. The actual figures may serve to make the point clearer, and are as follows:—

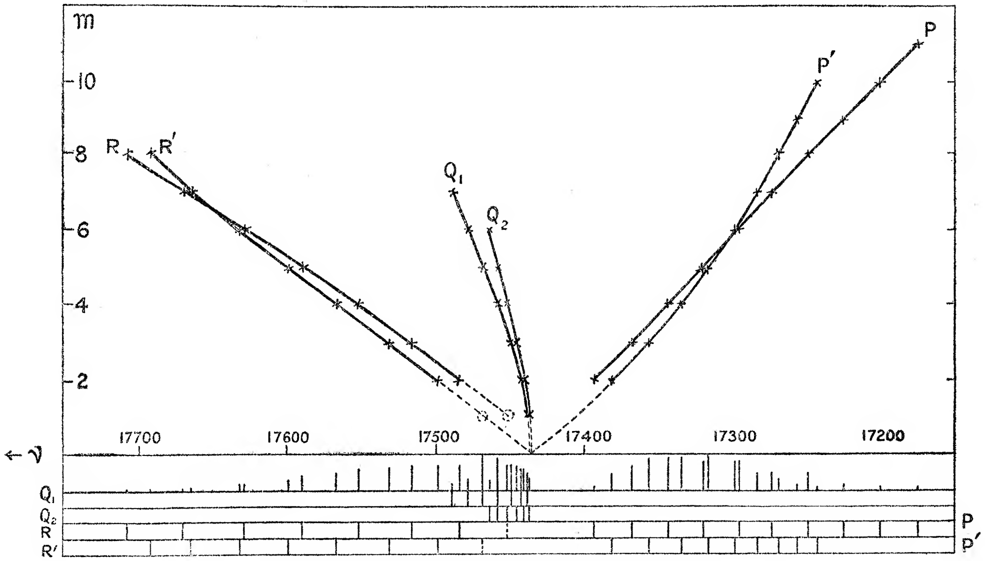

Fig. 4.—Helium band at λ 5730.

$Q_1(0) = 17437{\cdot}3, \qquad Q_2(0) = 17436{\cdot}4.$

$P(0) = 17453{\cdot}1, \quad c_0 = 16{\cdot}2, \quad \therefore \nu_0 = 17436{\cdot}9,$

$R(0) = 17420{\cdot}6, \quad c_0' = 15{\cdot}3, \quad \therefore \nu_0 = 17435{\cdot}9,$

$P'(0) = 17437{\cdot}3, \quad c_0 = 15{\cdot}0, \quad \therefore \nu_0 = 17422{\cdot}3,$

$R'(0) = 17408{\cdot}4, \quad c_0' = 13{\cdot}5, \quad \therefore \nu_0 = 17421{\cdot}9.$

The numbering of P′ and R′ is here not the same as in the Tables and figure, but that appropriate to the above view, so that the formula coefficients differ from those tabulated. The mean value of ν_0 derived from P and R, 17436·4, is identical with $Q_2(0)$, but the corresponding value from P′ and R′ is 17422·1, 15·2 units from $Q_2(0)$ and 14·3 from $Q_1(0)$. The discrepancy remains however the numeration is varied, and one is bound to conclude that there is a relative displacement between the Q series and the other two. Such a complication is to be avoided if possible, and a means of doing so is suggested by the results obtained in the preceding sections. We there established the existence of P′ series running approximately parallel to the

P series, but extrapolating to ν_2 instead of to $(\nu_0 + c_0)$. The apparently displaced P series of this group fulfils these conditions very closely (see Table VI and fig 4). Moreover, the associated R series also extrapolates to ν_0 and runs parallel to the normal R series, so that it must be regarded in a similar way. This leaves the extra Q series as the only quite anomalous feature of the band, and is therefore thought to be a much more satisfactory method of representation than that first proposed. The values obtained for ν_0 from P′ and R′ now become 17437·3 and 17436·8, in excellent agreement with those derived from Q_1, Q_2, P and R.

The existence of two Q series is a puzzling feature of this band, for they are so close together that it is impossible to say which of them is associated with the normal P and R branches. It is true that the mean ν_0 determined from the latter agrees exactly with $Q_2(0)$, but $Q_1(0)$ only differs from this by 0·9 unit, by no means a large discrepancy in the light of our experience in previous cases. Other evidence available is equally indecisive; for example, there appears to be some connection between P′ and Q_1 (evident from the coefficients), and also between R′ and Q_2 (see below), so that which is the normal and which the additional Q series remains in doubt. An attempt has been made to fit them both by one formula, in which m may have both positive and negative values, but this appears to be definitely impossible.

As mentioned above, there seems to be a relation between Q_1 and P′, in view of the remarkable similarity of the formulæ (except for the coefficients of m, which determine the type of the series), and again between Q_2 and R′. The latter appears when the differences $R'(m) - Q_2(m)$ are formed; these are found to be an approximately linear function of m, suggesting that if the formulæ had been exact the coefficients would have shown a similar correspondence to Q_1 and P′.

The question of missing lines is of much theoretical interest, and the position with regard to this band may be summarised thus :—

Series.	First observed line.	Remarks.
R	$m = 2$	R (1) would fall exactly on Q_2 (4), but the intensity of the latter seems normal.
Q_1	$m = 1$	The vertex of the parabola representing this series is nearer $m = -1$ than $m = 0$, which suggests that the first observed line may be $m = 2$.
Q_2	$m = 1$	The numeration here seems fairly well established.
P	$m = 2$	P (1) is definitely absent.
R′	$m = 2$	R′ (1) may be present, as it would fall on Q_1 (5), which shows a large residual, and is abnormally strong.
P′	$m = 2$	P′ (1) is definitely absent.

The observations are thus in good accordance with the theory, which demands that P (1) and R (1) should be absent if Q (0) does not occur. The theoretical significance of the P′ and R′ branches is at present unknown, but it may be noted that in the bands λλ 6400 and 4546 the line P′ (1) is present, whereas here it is absent.

The initial and final values of the amount of inertia, calculated from the P and R branches as before, are $1{\cdot}71 \times 10^{-40}$ and $1{\cdot}80 \times 10^{-40}$ grm.-cm.^{2}. These are a little lower than the corresponding results for the other two bands, but of quite the same order, so that it is unnecessary to suppose that we are dealing here with quite another type of molecule. The structural differences between the bands may reasonably be attributed to a difference between the changes of internal configuration involved. No other band resembling λ 5730 has been detected on the plates available, which cover the region λλ 6500 to 3350, but there are several regions where detection might be difficult.

Discussion of Results.

It has been shown in the preceding sections that the quantum theory of band spectra is capable of accounting in a very simple manner for the structure of the helium bands under consideration. Moreover, it explains their unusual appearance as due to an unusual intensity distribution necessarily resulting from the low atomic weight of helium. But the agreement with observation is not perfect; deviations from the parabolic formulæ demanded by the theory are commonly met with in band series, and are in fact exceptionally large in the case of these helium bands. The observational evidence in favour of the theory is very strong, and its general validity can hardly be questioned, but it should be capable of modification or extension in order to take into account these deviations, or perturbations, as they have hitherto been called.

The general character of the perturbations is most clearly seen when the wave-number intervals between successive lines of a series are plotted against the corresponding values of *m*, the rotation quantum number characterising a given line. If the theoretical formulæ held exactly a straight line would thus be obtained, and we may roughly estimate the magnitude of the perturbation by the extent to which the graph departs from linearity. The general result which emerges from an examination of these curves is that the perturbation increases with *m*, and usually more rapidly for higher values of *m*. In fact, in several cases the interval reaches a maximum, and begins to diminish just as the series fades out. A similar tendency has been noted in the case of other bands,* but only for much larger values of *m* than in the present case.

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* *E.g.*, Birge, ‘Astrophysical Journal,’ vol. 46, p. 92 (1917).

This feature of the perturbation immediately suggests as a possible cause the deformation of the molecule due to centrifugal force. In order to form an opinion as to whether the latter is likely to be large enough to produce the observed effects we may make a rough calculation as follows :—

Assuming two similar nuclei each of mass M at a normal distance $2r$ apart, the moment of inertia about an axis perpendicular to and bisecting the line joining them is I (say) $= 2\mathrm{M}r^2 = \frac{mh}{2\pi\omega}$. The centrifugal force on either

$$= \mathrm{M}\omega^2 r = \mathrm{M}r\left(\frac{mh}{4\pi \mathrm{M}r^2}\right)^2 = \frac{m^2h^2}{16\pi^2\mathrm{M}r^3}.$$

Now from the values for I already obtained, which average about $1 \cdot 8 \times 10^{-40}$, and taking $\mathrm{M} = 7 \times 10^{-24}$ (mass of helium atom) the value of $2r$, the distance apart of the nuclei $= 2\sqrt{\mathrm{I}/(2\mathrm{M})} = 0 \cdot 72 \times 10^{-8}$ cm. Substituting this value, the centrifugal force comes out as $m^2 \times 8 \times 10^{-7}$ dyne. We cannot directly determine the effect of this, since we are ignorant of the law of the attractive force binding the atoms, but we can perhaps gain some idea of its relative importance by comparing it with the force of repulsion between the two nuclei, which will be of the same order as the attractive force. Assuming a double charge on each, *i.e.*, setting an upper limit to the force, the latter will be about $1 \cdot 8 \times 10^{-2}$ dynes. This is about 20,000 times the centrifugal force due to a one-quantum rotation state, but only 200 times that called into play when the rotation is 10 times as fast (corresponding to the last observed lines in the present bands). The known instability of the molecules emitting the bands under discussion lends support to the conclusion that for the larger values of m here encountered the centrifugal force may quite possibly be great enough to cause an appreciable deformation of the molecule, with consequent deviations from the theoretical formulæ for the wave-numbers.

It is interesting to note, in passing, that the above considerations may serve to explain the relatively large deviations in the case of helium as due to the relatively small mass and size of the molecules, together with their unstable character. Larger and heavier molecules will experience smaller centrifugal forces for corresponding values of the rotation quantum, and if further they are more stable, will be less deformed in proportion.

Such a deformation may affect the radiated frequency in one (or both) of two ways, which correspond to the two terms composing the expression for the energy of the molecule, namely, the internal energy (comprising K.E. and P.E. of the nuclei and electrons), and the rotational energy. In other words, either ν_0 or I, or both, may vary with m. In the absence of any precise knowledge of the molecular structure we cannot expect to account in detail for the observed facts, but it seems possible to draw some general conclusions which are not without interest.

Whatever the exact effect of the supposed centrifugal forces, the energy of a molecule will depend partly upon its internal configuration and partly upon the rotation quantum number. Let the energy prior to a configuration change be $h\mathrm{F}(m)$ and that subsequent to the change be $hf(m)$. Then, assuming the three series to originate in the manner already described, we should have

$$\mathrm{R}(m) = \mathrm{F}(m)-f(m-1),$$

$$\mathrm{P}(m) = \mathrm{F}(m-1)-f(m),$$

$$\mathrm{Q}(m) = \mathrm{F}(m)-f(m),$$

also

$$\mathrm{Q}(m-1) = \mathrm{F}(m-1)-f(m-1).$$

Whence the following relation should be satisfied:—

$$\mathrm{R}(m)+\mathrm{P}(m) = \mathrm{Q}(m)+\mathrm{Q}(m-1).$$

This combination principle, which is due to Heurlinger, has been tested for a number of bands; in some cases it appears to hold exactly (*e.g.*, for hydrocarbon band λ 4300), but in others (*e.g.*, H_2O, MgH_2), a deviation appears for large values of m. The extent to which it applies to the bands λλ 6400 and 5730 may be seen from Table VII, which shows the values of $(\mathrm{R})\,m+\mathrm{P}(m)/2$ and $\mathrm{Q}(m)+\mathrm{Q}(m-1)/2$, together with the differences between these quantities. In the case of λ 5730, where there are two Q series, the test has been made on each in turn. The relation is evidently far from exact in these cases, and the departure from it is quite systematic, increasing in general with m. Since the combination principle would not be invalidated by the existence of deformation due to centrifugal force, we conclude that the latter is not competent to produce the whole of the observed deviations from the theory.

The intensity distribution in band series is a point of some theoretical interest, since it leads to an estimate of the distribution of rotational velocities amongst the molecules. The plates on which the present work is based are not very suitable for intensity estimations, as all the stronger lines are considerably over-exposed, but so far as can be judged the intensity distribution is fairly normal. That is to say, there is a maximum two or three lines from the beginning of the series, then four or five lines of fairly uniform intensity, and finally a rather rapid falling off as the end of the series is approached. Having regard to the unusually small number of lines developed, this is comparable with the distribution in "ordinary" band series, except that the latter do not in general fade out so suddenly. The cause of this peculiarity in the helium bands may be that for the higher rotational velocities the molecule is approaching an unstable condition.

If it were merely a question of whether the molecules possessing these larger velocities were sufficiently numerous to be detected one would expect a more gradual falling off in intensity.

Table VII.—Test of Combination Principle.

Band λ 6400.

m.	I. $\frac{R(m)+P(m)}{2}$	II. $\frac{Q(m)+Q(m-1)}{2}$	I–II.
2	15624·30	15623·14	+1·16
3	23·30	21·57	+1·73
4	21·82	19·21	+2·61
5	19·68	15·92	+3·76
6	16·88	11·74	+5·14
7	13·12	6·71	+6·41

Band λ 5730.

m.	III. $\frac{R(m)+P(m)}{2}$.	IV. $\frac{Q_1(m)+Q_1(m-1)}{2}$.	V. $\frac{Q_2(m)+Q_2(m-1)}{2}$.	III–IV.	III–V.
2	17438·72	17441·37	17439·63	−2·65	−0·91
3	42·39	46·40	43·65	−4·01	−1·26
4	47·68	53·38	48·75	−5·70	−1·07
5	54·45	62·32	54·43	−7·87	+0·02
6	62·14	72·50	60·10	−10·36	+2·04
7	70·40	83·40	—	−13·00	

Note.—In the case of λ 6400 the differences (I–II) would be considerably smaller if the Q series were numbered one higher throughout, but would still show a strong systematic variation. The agreement between the empirical and theoretical formulæ for this series, however, supports the numeration adopted.

The differences III–IV would also be reduced by a similar change of numeration, but again the systematic variation would remain. In this case the coefficients of the empirical formula for Q_1 seem to suggest that such a change may be necessary.

This question of the distribution of angular velocities has been investigated theoretically by Kemble,* who finds that the intensity maximum of the band should correspond to an angular velocity ω determined by the relation $I = RT/\omega^2 N$, where R is the gas constant, T the absolute temperature, and N the number of molecules per gramme-molecule. By substituting $I\omega = mh/2\pi$ this reduces to

$$m^2 = \frac{4\pi^2 IRT}{h^2 N} = \frac{RT}{hN \,.\, 2c_0} \text{ since } c_0 = \frac{h}{8\pi^2 I}$$

$$= \frac{0{\cdot}68T}{2c_0} \text{ approx., when } c_0 \text{ is expressed in cm.}^{-1}.$$

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* 'Phys. Rev.,' vol. 8, p. 689 (1916).

For the helium bands $2c_0$ is about 30 cm.$^{-1}$; T is not known, but is not likely to be much above room temperature. Putting it at 300° K we find $m = 2{\cdot}6$, *i.e.*, the maximum should occur at about the second or third line, or perhaps a little farther from the beginning of the series if T has been under-estimated. The intensity estimates are too rough to permit of an exact verification, but the predicted result is of the right order.

One difficulty, hitherto passed over, calls for consideration, namely the assumed existence of a molecule of helium; it is a necessary assumption, for the moments of inertia found are much too large to refer to a helium atom. In this connection Lenz* has made the plausible suggestion that when one of its electrons is close to the nucleus and the other far removed (*i.e.*, in an outer orbit) the helium atom is approximately equivalent to a hydrogen atom so far as electrical forces are concerned, and two such atoms may unite to form an unstable helium molecule of similar type to the hydrogen molecule. Whatever the precise constitution of the helium molecule, there is no doubt of its instability. Its development seems to require special conditions of pressure and electrical excitation, and is greatly favoured by absence of all impurities.†

Granted that a molecule of helium may exist, the theory accounts for the bands as arising from a simultaneous change of internal and rotational energy. The nature of the former change cannot be directly inferred from the data here presented, but it is probably a change in the configuration of the electrons, since the resulting frequencies ν_0 are of the same order as for Fowler's series of doublet bands, which are distributed according to the ordinary law of line series. If nuclear vibrations can occur in this case, which the instability of the molecule renders somewhat doubtful, they are likely to be of a lower order of frequency, and may be expected to give rise to bands in the near infra-red region. It is hoped that a search for these may be undertaken in the near future. The pure rotation spectrum corresponding to the present bands will lie in the far infra-red, round about 100μ, and will consequently be difficult to observe.

Application of Results.

It is thought that the results obtained may be of service in several ways. The first application will naturally be to the remaining bands in the spectrum, although these appear to show some marked differences in structure. They are nearly all included in Fowler's doublet series; the double heads are probably of Q type, and are accompanied in each case by a P series, but not by an R series, so far as can be ascertained by inspection. The separation of the two heads is much greater than in the case of the λ 5730 Q series.

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* 'Verh. d. D. Phys. Ges.,' vol. 21, p. 632 (1919).

† Some interesting observations in this connection will be found in a paper on "Radiation and Ionisation in Helium," by Horton and Davies, 'Phil. Mag.,' vol. 42, p. 746 (1921).

There is little doubt that the secondary spectrum of hydrogen is due to the hydrogen molecule, and it may therefore be expected to show the general features of a band spectrum together with some of the special features which distinguish the helium bands. The smaller moment of inertia which we may assume the hydrogen molecule to possess, however, should lead to a larger frequency interval between successive members of a series, and probably also to the development of a less number, although in this connection the relative stabilities of the two molecules will have an influence. Either factor would make the series relationships more difficult to detect, but a beginning has already been made,* and it seems reasonable to hope that further progress may be facilitated by the present observations.

The infra-red absorption bands of HF, HCl and HBr,† which have been the subject of much discussion during the last few years, present features which it is interesting to examine in the light of the present results. They appear to consist of P and R type series (but no Q branch) of a normal character, except that only one line is missing from the middle of the band, whereas on the simple theory missing lines should occur in pairs. Kratzer‡ has put forward an explanation of this, and reaches the conclusion that in emission bands the line due to the transition 1 → 0, *i.e.*, R(1), should be missing, and in absorption bands that corresponding to 0 → I, *i.e.*, P(1). It remains to be seen whether this is confirmed by experience in the case of these bands, for no adequate data relating to their emission characteristics are available, but it certainly does not appear to hold in the case of helium. An alternative possibility which is suggested by the present results is that these absorption bands may be of the P′ and R′ type, in which case the missing line would be $P'(0) = R'(0) = \nu_0$. This would account for the peculiarity referred to, but until some theoretical explanation of the P′ R′ system is forthcoming the question must be left open.

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* Fulcher, 'Astrophysical Journal,' vol. 37, p. 60 (1913).

† Imes, 'Astrophysical Journal,' vol. 50, p. 251 (1919); Colby and Meyer, 'Astrophysical Journal,' vol. 53, p. 300 (1921).

‡ 'Z. f. Physik,' vol. 3, p. 289 (1920).

Summary.

Grating photographs of three of the principal helium bands have been measured and analysed, with the following results :—

(1) Tables showing wave-lengths, intensities, wave-numbers and allocation to series are given, also diagrams exhibiting the structure of the bands.

(2) The chief features of their structure are shown to be accounted for by the quantum theory of band spectra, a brief *résumé* of which is given.

(3) In each of the three bands a new type of series is found which, although closely related to the others, has not yet received a theoretical explanation. Other departures from the theory are also noted.

(4) It is concluded that the spectrum is due to an unstable helium molecule, having a moment of inertia of about $1{\cdot}8 \times 10^{-40}$grm.-cm.^{2}

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On the Molecular Scattering of Light in Water and the Colour of the Sea.

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1. *Introduction.*

The theory that the light of the sky owes its origin and colour to diffraction by the molecules of the atmosphere is now established on a firm experimental basis by the brilliant work of Cabannes and of Lord Rayleigh on the scattering of light by dust-free gases, and by the measurements of the transparency of the higher levels of the atmosphere in the visual region of the spectrum, which have yielded results in close agreement with the calculated values. It is the purpose of the present paper to point out the part played by molecular diffraction in another of the great natural optical phenomena, that is, the colour exhibited by large masses of clear water when